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<b>13. ABSTRACT (Maximum 200 Words)</b> This report accounts for the major scientific accomplishments of the above project from May 2002 to November 2004. The focus of this proposal was the development of methods and techniques for the assembly of 3-D nanoparticle lattices using a variety of nanoparticles and novel DNA-driven assembly techniques. Microorganisms and diatoms were used as templates for the hierarchical assembly of ordered 3-D nanostructures, and DNA-linked nanoparticles were shown to form organized lattices in aqueous medium. In addition applications were developed to use diatoms as bio-templates for new materials. The self-organization of gold nanoparticles modified with DNA led to the assembly of supramolecular gold nanoparticle assemblies with unique physical characteristics. These novel supramolecular gold nanoparticle structures have potential applications as novel biodetection systems displaying properties distinct from those of the single gold nanoparticles. Finally, hybrid organic-inorganic nanorods and nanowires were synthesized, and the electrical properties of these structures were studied. Newly synthesized nanowires can self-assemble into "mushroom", "sheet" and "tubular superstructures", a process that is driven by the strong interactions between the polymer domains. The diameter and length of these novel 3-D complexes are determined by individual nanowire components. In the context of an integrated microelectrode device, these nanorod structures displayed resistor- or diode-like behavior, which suggests potential applications of these devices in areas as diverse as solar energy conversion.				
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## **AFOSR Final Report**

### **BIOINSPIRED MATERIALS FOR COMPACT POWER STRUCTURES**

Grant Number: F49620-02-1-0180

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## **Bioinspired Materials for Compact Power Structures**

### **OBJECTIVES**

The objectives of this project as described in the original research proposal were as follows:

1. Develop core-shell methodologies for functional nanoparticles and rods modified with DNA and protein-based scaffolding materials.
2. Use novel nanocomposite materials for biology-based assembly strategies.
3. Characterize and evaluate the electrical, electrochemical, magnetic and optical properties of 3-D structures prepared via novel assembly strategies developed as part of this project.

### **EXECUTIVE SUMMARY**

This project focused on the development of methods and techniques for the assembly of 3-D nanoparticle lattices using a variety of nanoparticles and novel DNA-driven assembly techniques. It was envisioned that these techniques would make it possible to investigate chemically, electrochemically and photochemically stimulated electron and ion flow in the context of a colloidal crystal comprised exclusively of nanoparticle materials.

Over the two and a half years of this project, significant progress was made towards all three objectives as listed above. Microorganisms and diatoms were used as templates for the hierarchical assembly of ordered 3-D nanostructures, and DNA-linked nanoparticles were shown to form organized nanocrystals in an aqueous medium. In addition applications were developed to use diatoms as bio-templates for new materials. The self-organization of gold nanoparticles modified with DNA molecules led to the assembly of supramolecular gold nanoparticle assemblies with unique physical characteristics. These supramolecular gold nanoparticle structures have potential applications as novel biodetection systems displaying properties distinct from those of the single gold nanoparticles.

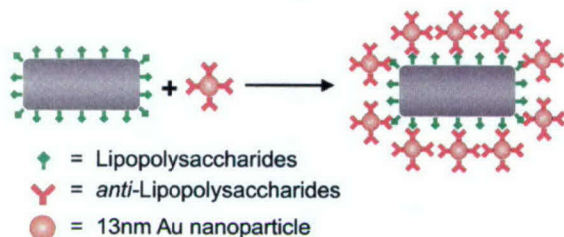
Finally, hybrid organic-inorganic nanorods and nanowires were synthesized, and the electrical properties of these structures studied. Newly synthesized nanowires can self-assemble into "mushroom", "sheet" and "tubular superstructures", a process that is driven by the strong interactions between the polymer domains. The diameter and length of these novel 3-D complexes are determined by individual nanowire components. In the context of an integrated microelectrode device these nanorod structures displayed resistor- or diode-like behavior, which suggests a variety of potential applications for these devices.

The project has been particularly productive and has led to the publication of nine manuscripts in peer-reviewed journals, several patent applications, transitions to industry, and several awards.

## ACCOMPLISHMENTS

### 1. Novel Nanocomposite Materials as Building Blocks for Assembly Strategies Using Biological Templates

#### 1.1. Hierarchical Assembly of Nanoparticles using Bacteria as Templates



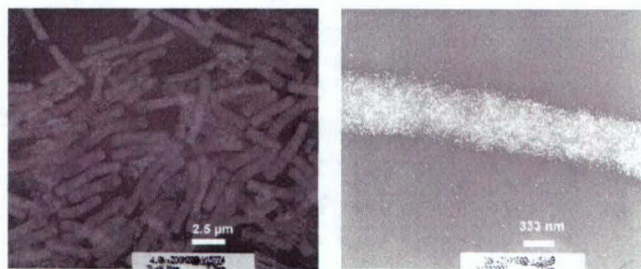
**Figure 1:** Microorganisms as bio-templates for 3-D assembly of gold-nanoparticles.

be genetically manipulated such that particular functional groups are expressed, which interact with or nucleate nanoparticles. An ideal biological template would be one that could be chemically modified in a controlled and versatile manner using conventional bench-top methods so that nanostructured material can be easily analyzed. Both of these strategies have been successfully explored using the structural motifs of bacteria and diatoms as bio-templates for the 3-D assembly of nanoparticles. A schematic representation of the assembly procedure is shown in Figure 1.

In this particular case lipopolysaccharide (LPS), a key component of the cell wall of gram-negative bacteria was used as a platform for the assembly of different nanostructures (Figure 2). When bacteria were coated with gold nanoparticles conjugated to anti-lipopolysaccharide antibodies, micrometer sized rods and spherical particles were assembled. Alternatively coating microorganisms with anti-LPS antibodies conjugated to gold nanoparticles covered with single-stranded DNA made it possible to use bacteria as templates and building blocks for hierarchical assembly strategies. While the anti-LPS antibodies anchor the gold particles to the bacterial cell surface, the single-stranded DNA molecules facilitate the deposition of new layers of DNA-functionalized nanoparticles and tie individual bacteria into hierarchical structures.

Currently a “microorganism-tool-kit” is compiled to assemble macroscopic bio-templates with domains defined by the size and shape of a particular microorganisms, and nanoscopic domains controlled by the size and type of nanoparticles used to coat the microorganisms.

Microorganisms have been used as versatile templates for the assembly of large, functional architectures from nanoparticle building blocks. Two techniques were explored: bacteria were used either to non-specifically adsorb nanoparticles or as a template for the nucleated growth of the latter. Alternatively the template organism can

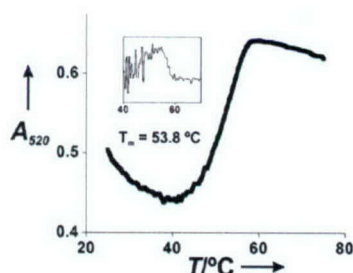


**Figure 2:** TEM images of the assembly of gold nanoparticles using rod-shaped bacteria.



## 1.2. Hierarchical Assembly of Nanoparticles using Diatoms as Templates

Diatoms are a diverse class of unicellular algae with unique shapes and an intricate cell wall whose key component is silica. The silica shells are called frustules and are used to distinguish diatoms taxonomically. Frustules are composed of two valves, with one fitting within the other one and dimensions between 1 and 100  $\mu\text{m}$ . The intricate silica shells have made diatoms prime candidates for the assembly of prefabricated nanoparticles (Figure 3). During the course of this project it was shown that DNA, either unmodified or modified with a fluorescent dye, could bind covalently to diatoms, using basic glass-modification techniques (Figure 3). Modified diatoms were subsequently used as templates for the sequence-specific assembly of DNA-functionalized nanoparticles and

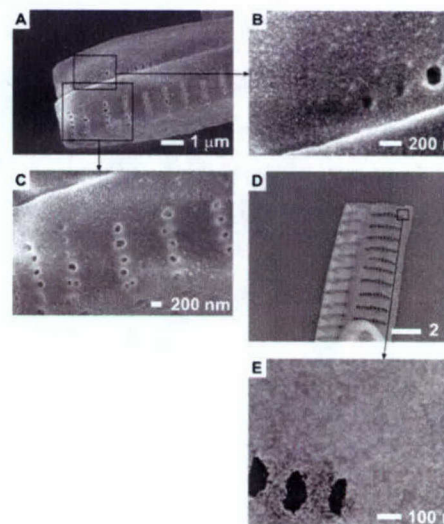


**Figure 4:** Release of DNA gold nanoparticles from diatom surfaces. Measuring the absorbance at 520 nm monitors the release process.

for the programmed assembly of patterns of multiple layers of nanoparticles. Interactions between individual diatoms and gold nanoparticles, directed and controlled by sequence-specific interactions between oligonucleotide sequences on the diatom surface and complementary sequences on the gold nanoparticle, led to the assembly of gold nanoparticles on the diatom surface (Figure 5). No assembly was observed when nanoparticles modified with non-complementary DNA were used.

In general, the sequence-specific assembly properties of functionalized diatoms mediated by complementary DNA strands can be applied to assemble hierarchical structures and thus to confer sophisticated properties to the templated materials in a reversible manner (Figure 4). As nanoparticles are attached to the

diatom surface in a reversible manner via duplex DNA, raising the temperature beyond the melting point of the duplex will release the nanoparticles from the template. This release process can be monitored by UV-VIS spectroscopy as the characteristic nanoparticle surface plasmon band at 520 nm increases with temperature (Figure 4). The sharp melting transitions, which are a consequence of the cooperative melting effect of aggregates of DNA-functionalized nanoparticles, corroborated the dense surface coverage observed by electron microscopy. Monolayers of DNA-functionalized gold particles of 13 nm size melt over a range of 5°C, whereas duplex DNA structures composed of complementary single-stranded DNA between gold nanoparticles and individual diatom surfaces melt over a temperature range of 8-10°C. It is believed that the irregular, undulating diatom surface decreases the net cooperative melting effect and thus causes the duplex DNA to separate over a broader temperature range.

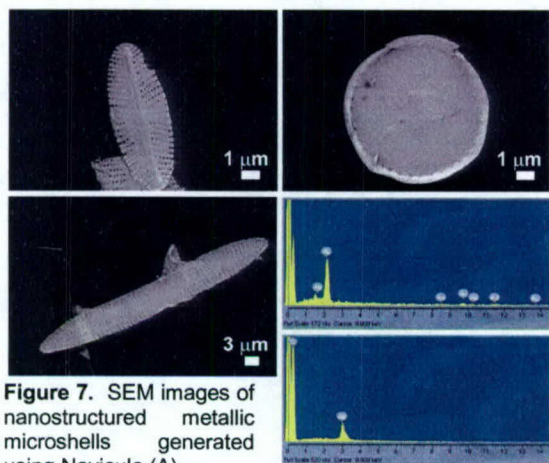


**Figure 5:** TEM (A-C) and SEM (D, E) images of *Synedra* diatoms coated with DNA-modified gold nanoparticles.



Unlike the surface structures of other biological templates, diatoms have cell walls that exhibit remarkable species-specific nanoscopic details including pores, grooves, and ridges that currently cannot be reproduced using conventional material

fabrication techniques. These unique characteristics in conjunction with the distinctive properties of nanomaterials, will be exceptionally useful for a range of applications in catalysis, optics, and Surface Enhanced Raman Scattering (SERS). Currently studies are under way to investigate these novel nanomaterials as substrates for SERS and methods are being developed to arrange functionalized diatoms into well-ordered macroscopic arrays. This work formed the basis for our renewal proposal.



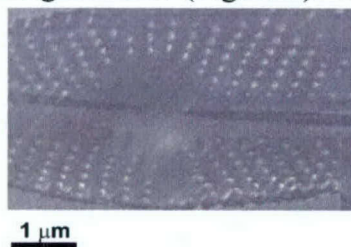
**Figure 7.** SEM images of nanostructured metallic microshells generated using Navicula (A),

Thalassiosira (B), and Synedra (C) diatom templates. EDS spectrum Au (D) and Ag (E) coated Synedra after dissolution of the silica shell.

### 1.3. Diatoms as Lithography Masks for Novel Metal Nanostructures

In a different line of experiments applications were developed to use diatoms as bio-templates for the synthesis of new materials. For these studies, diatoms were deposited onto glass slides to form non-overlapping pseudo-monolayers onto which metals (Au, Ag, Pt, etc.) were dispersed. The metal-coated diatoms were subsequently released from the glass slide by sonication. During this process, two classes of novel materials were obtained.

One material is the intricate metal nanopattern of metal-coated diatom shells on the glass slide (Figure 6). When these shells are collected and the silica shell dissolved in



**Figure 6.** SEM images of silver nanopatterns generated using diatom masks.

HF, a metallic microshell with the imprinted nanoscopic features of the diatom is released (Figure 6). This is the second novel material produced in this innovative nanofabrication process. Both of these new materials are generated using a single process and the intricate patterns and nanoscopic features of each can be reproduced cheap and in bulk quantities. The optical properties of individual structures will be further analyzed by near-field scanning optical microscopy (NSOM) and confocal Raman microscopy in order to determine which structures

may be useful as SERS substrate. Currently methods are being developed to use diatom monolayers as templates to fabricate arrays onto which a variety of metals can be deposited.

The potential metal nanostructures that can be generated using this technique are numerous and only limited by the availability of diatom species that can be used as template in this process. The use of different diatom species as lithography masks offers the potential to fabricate a whole range of novel metal nanostructures by replicating a naturally occurring biological template.



## 2. Core-Shell Methodologies for Functional Nanoparticles and Rods Modified with DNA and Protein-Based Scaffolding Materials

### 2.1. Novel DNA Micelles as Building Blocks for the Assembly of 3-D Structures

DNA amphiphile molecules can self-assemble in aqueous solutions into spherical micelle structures (Figure 8) in a manner similar to amphiphilic block copolymer analogues. During this project a method to synthesize DNA amphiphiles through direct coupling of a hydrophobic polymer phosphor-amidite to a hydrophilic DNA chain using solid phase DNA synthesis tools was developed (Figure 9).

3-D networks were assembled from solutions of DNA micelles and gold nanoparticles modified with a complementary DNA strand upon mixing of the

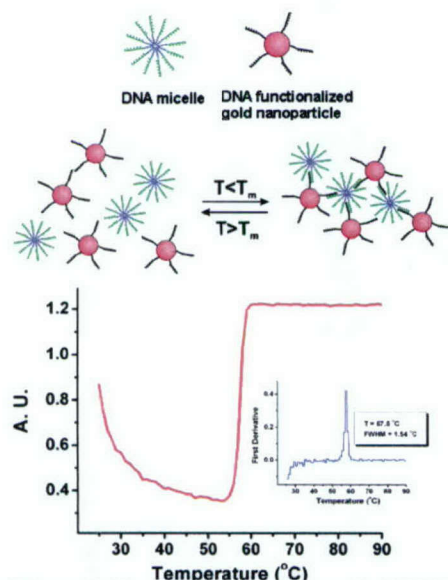


Figure 8: Formation of 3-D network of DNA micelles and gold nanoparticles.

have been non-covalently modified with amphiphilic DNA. Figure 8 shows an AFM image of the 3-D network produced by polystyrene-DNA amphiphiles and gold nanoparticles.

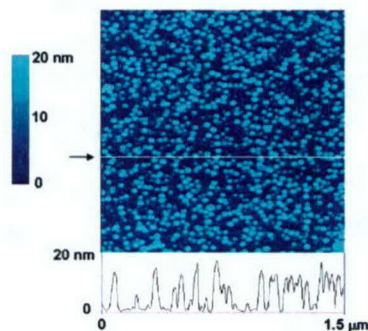


Figure 10: AFM image of spherical micelle structures assembled from DNA amphiphilic building blocks.

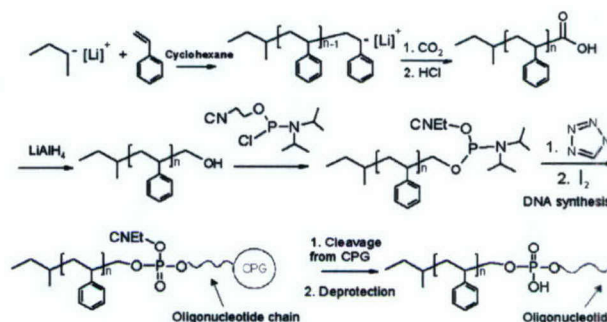


Figure 9: Synthetic route to polystyrene-DNA amphiphiles.

two components. This reversible, temperature-dependent assembly process is triggered by hybridization of the two complementary DNA strands and can be reversed by increasing the temperature (Figure 8). As the recognition characteristics of 3-D micelles composed of DNA amphiphiles are directly determined by the hydrophilic DNA component, these molecules can be used as building blocks for the assembly of 3-D structures through sequence-specific DNA hybridization. In addition these molecules can also be used as novel encapsulation reagents to render hydrophobic nanomaterials soluble in aqueous solutions and to confer recognition properties.

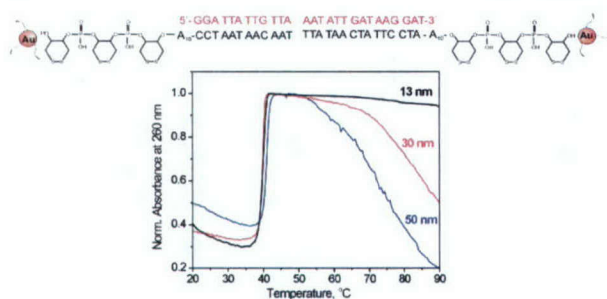
This potential application of amphiphilic DNA micelles has been confirmed in preliminary experiments with single wall carbon-nanotubes that

### 2.2. Assembly of Supramolecular 3-D Lattice Structures

Nanomaterials are an interesting class of materials with distinct chemical and physical properties. As the size of the constituting particles decreases, the physical and chemical properties change as well.



Nanocrystal superlattices (NCS), sometimes also referred to as colloidal crystals, represent a new class of nanomaterials that are composed of nanoparticle building blocks

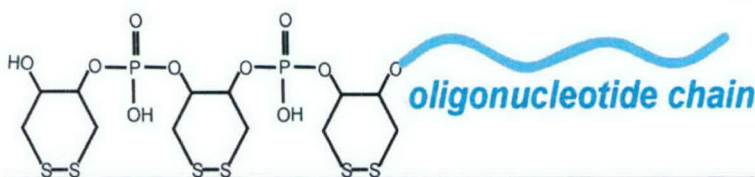


**Figure 11:** Melting of gold nanoparticles aggregates stabilized by a disulfide-containing DNA.

of novel condensed matter. These building blocks are organized into long ordered arrays, the formation of which is favored by the size and shape uniformity of the particles. As a class they are distinguished from other nanomaterials through unique collective properties that are distinct from those of the singular nanoparticles.

Though it is possible to reproducibly synthesize monodisperse nanoparticles in organic solvents that stabilize particles mainly through van der Waals and steric forces, there are no reports that describe the synthesis of nanoparticles in aqueous media, where the predominant

stabilization forces are electrostatic. Synthesis of nanoparticles in aqueous solutions is a particularly challenging problem since nanoparticles prepared in an aqueous medium have broader size and shape

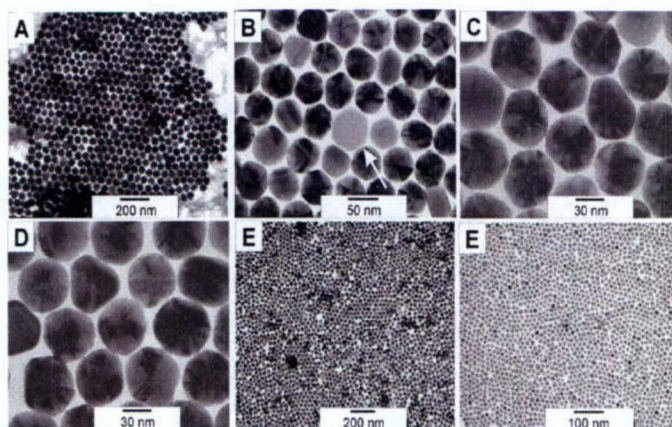


**Figure 12:** Disulfide-containing DNA used for stabilization of different size gold nanoparticles.

distribution compared to those synthesized in organic solvents. Studies of nanoparticles in aqueous media are particularly valuable as they allow the investigator to systematically analyze the physical properties of superlattice structures and to explore potential applications in the areas of biomolecule detection and sensing devices.

Studies of the self-organization of gold nanoparticles modified with DNA molecules in aqueous environments revealed that a combination of the DNA recognition properties and the unique physical characteristics of the supramolecular gold nanoparticle assemblies led to novel biodetection systems that displayed properties distinctive from those of the single gold nanoparticles.

A novel phosphoamidite, containing a disulfide was used to modify DNA at the 3'- or 5'-terminus with disulfide groups (Figure 12). When DNA modified in such a way was used to stabilize gold nanoparticles of 13 nm, 30 nm and 50 nm,



**Figure 13:** TEM micrographs of nanocrystal superlattices formed by DNA-functionalized gold nanoparticles. (A-D) 50 nm particles, (E) 30 nm particles (F) 13 nm particle. Note the particle organization despite differences in size and shape of the particles.



particle aggregates formed in which individual gold particles stabilized by DNA were connected by a DNA linker. The melting properties of these particle aggregates are characterized by sharp melting transitions, which are typical for DNA-functionalized gold nanoparticles and are attributed to cooperativity (Figure 11).

When gold nanoparticles stabilized by disulfide-containing DNA are deposited onto a support they will self-assemble into arrays of ordered, hexagonal structures regardless of differences in size and shape (Figure 13). This self-organization, to our knowledge, is the first example where the uniformity of the nanoparticle core does not drive the organization of nanocrystals.

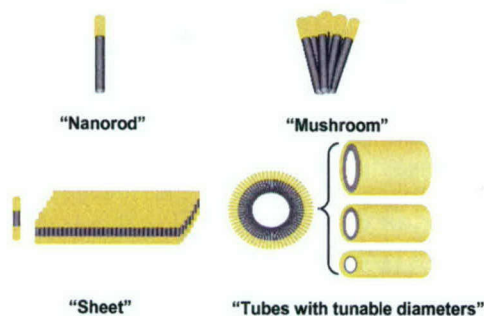
Control experiments with DNA linked to nanoparticles without rigid S-S moieties showed no superlattice formation. This suggests that the orientation of the ligands with respect to the nanoparticle surface plays an important role in facilitating the organization of the particles into ordered structures.

### 3. Electrical, Electrochemical, and Optical Characterization of 3-D Structures Fabricated Using Novel Assembly Strategies

#### 3.1. Fabrication and Characterization of Multifunctional Electrical Devices from Rod-Shaped Nanostructures

During the course of this project a technique to synthesize multi-component 1-D nanostructures composed of both organic and inorganic material building blocks was developed.

1-D nano- (or submicron-) structures, such as rods and wires, which have potential applications as meso-scale optical, electronic and optoelectronic building blocks, have been synthesized and assembled in a controlled manner. The synthesis pathway that leads to composite nanowires entails manufacturing gold nanowires



**Figure 14:** Assemblies of gold-pyrrole nanorod building blocks. The two building materials can be distinguished as bright gold and dark polymer fragments.

composed of gold and a conducting polymer. These nanowires are fabricated in a porous aluminum template through electrochemical deposition of gold, followed by electrochemical polymerization of pyrrole monomers and subsequent release of the nanowires from the templates. The length of the individual inorganic and organic blocks can be controlled by the total charge passed during the synthesis. Subsequently nanowires will self-assemble into “mushroom”, “sheet” and “tubular” 3-D superstructures, a process that is driven by the strong interactions between the polymer

domains. Diameter and length of these novel 3-D complexes are determined by individual nanowire components (Figure 14).

Using this technique countless domain-segmented metal-polymer nanowires can be prepared. As shown in Figure 15a, the newly synthesized nanorods organize into unique bundles of nanowires, of “hard-mushroom” shape. The highly ordered polymer chains along the polymer fiber wall induce strong  $\pi$ - $\pi$  stacking interactions among



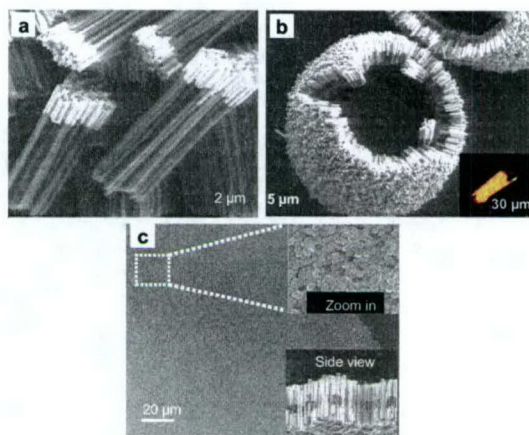
polymer rods, which are believed to be the driving forces of the assembly process. These strong  $\pi$ - $\pi$  stacking interactions cannot be compensated by the weak van der Waals interactions between the gold components.

The self-assembly of nanorods is thermodynamically favored as the entropy of this process increases, while at the same time the excluded volume per rod in the superstructure is minimized. These principles make it possible to design 3-D tubular architectures composed of gold-polymer wires. Moreover, the strong polymer interaction and volume difference between gold and polymer domains can induce curved feature formation. A range of nanowires, each 4~5  $\mu\text{m}$  in length and composed of gold and polymer building blocks of different domain size and varying gold/polymer ratios of 2/8, 6/4, and 8/2 have been synthesized.

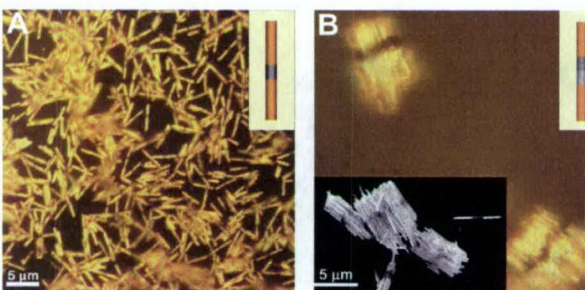
Figure 15b displays a representative 3-D tubular superstructure of  $\sim 29 \mu\text{m}$  in diameter composed of nanowires of a gold/polymer ratio of 6/4. "Flat sheet" superstructures have been designed by inserting polymer domains between the gold rod components (Figure 15c). The close-packed arrangement is clearly seen in the insets, which depict top and side views.

By controlling the composition as well as the length of the individual blocks comprising a single nanorod it was possible to obtain multi-component rod-like nanostructures with very specific electronic properties. In a typical experiment, segmented metal-polymer nanorods ( $d=324 \text{ nm} (\pm 32)$ ) were synthesized by electrochemical deposition of gold, silver or cadmium onto aluminum templates, followed by electrochemical polymerization of pyrrole (Ppy). By monitoring the charge applied during the electrodeposition process, blocks of specific length could be synthesized. The end products of this process are multi-component rod structures with specific, tailored electronic properties.

Figures 16A and B illustrate three-segment (Au-Ppy-Au) and four-segment (Au-Ppy-Cd-Au) nanorods. In the case of the Au-Ppy-Au system, dark Ppy domains sandwiched between two bright segments of gold can be seen (Figure 16A). Figure 16B illustrates the optical microscopy and FESEM images of Au-Ppy-Cd-Au rods. Ppy and Cd deposits are seen as dark and white segments, respectively, sandwiched between gold fragments at both ends. While the central polymer blocks determine the electrical properties (conductivity or resistivity) of the hybrid rod system, the two Au end blocks



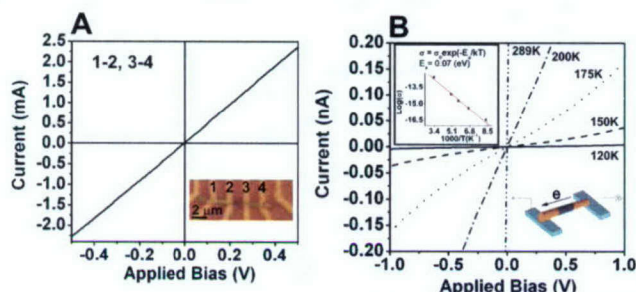
**Figure 15:** Assembly of Nanorods: (a ) mushroom, (b) tubular and (c) plate aggregates.



**Figure 16:** Optical microscope images of Au-Ppy-Au (A) and Au-Ppy-Cd-Au rods (B). The lower left inset shows the corresponding field emission electron microscopy (FESEM) image.



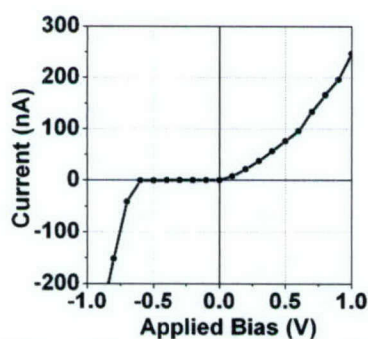
function as electrical contact pads to the macroscopic circuit. For examples, three-segment (Au-Polypyrrole-Au) “resistor” nanorods show the typical behavior of a moderately doped p-type semiconductor where the Ppy block makes an Ohmic contact between the Au-Ppy junctions. Four-segment (Au-Ppy-Cd-Au) “diode” nanorods show a current rectifying behavior at room temperature due to the formation of Schottky-like junctions at the Ppy-Cd interface in contrast to Ohmic junctions at the Ppy-Au interface.



**Figure 17:** (A) I-V measurement for gold blocks (1-2, 3-4) within a single nanorod (room temperature). Inset: Optical microscope image (mag. 1000X) of a single Au-Ppy-Au rod on prefabricated microelectrodes. (B) Temperature dependent I-V curves for measurements across electrodes 2 and 3. Upper left inset: Plot of  $\log \sigma(T)$  vs.  $1/T$ . The slope of the graph is determined by the activation energy ( $E_a$ ) which is  $\sim 0.07$  eV.

behavior at room temperature (Figure 17 A). Linear I-V plots over a voltage range of -1 to +1 V demonstrate Ohmic behavior. In contrast I-V measurements across the Ppy block of the Au-Ppy-Au nanorod (2-3 and 1-4 contacts) exhibit a linear response at room temperature, but behave in a non-linear fashion at low temperature ( $<175$  K). These are characteristics of a semiconductor (Figure 17B).

An analysis of the I-V plots and the corresponding electrical conductivities allows two important conclusions. While the central polymer blocks determine the electrical



**Figure 18:** I-V characteristics for a single Au-Ppy-Cd-Au rod at room temperature.

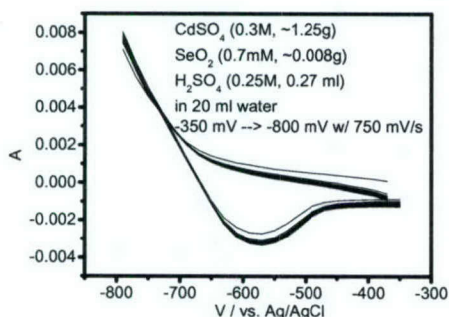
properties of the hybrid three-component system, the two Au blocks function as electrical connectors to the microscopic circuitry. As the temperature decreases, the I-V response of the Au-Ppy-Au nanorods becomes to some extent non-linear (Figure 17B) and the nanorods show Arrhenius-type temperature dependence, typical of thermally activated charge transport within a polymer block (Figure 17B inset).

I-V measurements on devices composed of single four-component Au-Ppy-Cd-Au rods exhibit “diode” behavior at room temperature (Figure 18). The typical response is asymmetric and non-Ohmic. In the forward bias, holes move from the Ppy to the Cd segment, due to a positive voltage on the adjacent Au block and negative potential on the Au block bordering the Cd segment. In reverse bias, current does not flow until the bias overcomes the breakdown potential ( $-0.61$  V). The turn-on voltage for these diode nanorods is approximately 0.15 V. The rectifying ratio (forward

Single nanorod devices were manufactured by depositing three-component Au-Ppy-Au nanorods on top of a microelectrode array. The electrical properties of these devices were characterized at different temperatures. Multiple individual microelectrodes make it possible to address a nanostructure electronically at different points along its long axis. The gold portions of the nanostructure (measured across contacts 1-2 and 3-4) exhibit linear I-V characteristics and bulk metallic



bias current/reverse bias current) is  $\sim 200$  at  $\pm 0.6$  V. The I-V characteristics of the Au-Ppy-Cd-Au nanorods at room temperature suggest that due to the difference in work

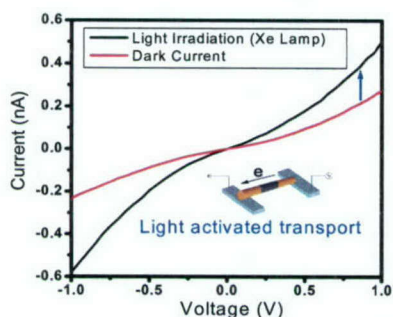


**Figure 19:** Cyclic Voltammetry (CV) plots of an aqueous mixture of Cadmium and Selenium precursors in an aluminum oxide template system. The current-potential curves show the deposition of CdSe.

functions of the polymer and the cadmium a Schottky-like junction is formed at the Ppy/Cd border. However, since the work function for the polymer and the gold are similar, an Ohmic junction is formed at the Ppy/Au interface. These experiments have shown that multi-component rod-like structures composed of metals, inorganic semiconductors and conducting polymers can be synthesized in an ordered, controlled manner via template-assisted in situ electrochemical deposition. Depending on the composition of the building blocks they will display either resistor- or diode-like behavior.

### 3.2. Applications for Multi-Component 3-D Rod-like Nanostructures

One potentially important application of the 3-D rod-like nanostructures described in the preceding paragraph is the conversion of solar energy at the mesoscopic length



**Figure 20-A:** I-V characteristics of a single Au-Cd-Se-Au nanorod (at room temperature). The increment of the light dependent conductivity became larger at higher ( $> 1.0$  V) bias voltage. The light dependent conductivity change is reversible.

scale, in particular the harvesting of light and its conversion to power microelectrical mechanical system (MEMS) devices. The manufacturing of rod-like “light harvesting” nanostructures relies on the idea of thin-film organic/inorganic solar cell structures.

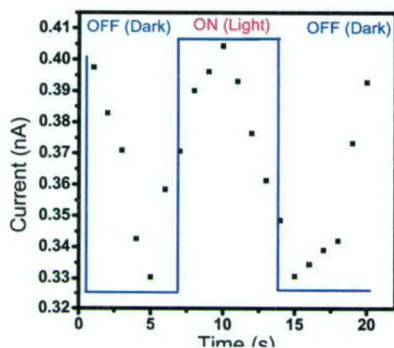
Four-component Au-CdSe-Au “photo detector” nanorods with a central segment of inorganic chromophores were manufactured. Figure 19 shows the in situ electrochemical deposition of CdSe via Cyclic Voltammetry (CV) inside a template system of aluminum oxide. Each cycle deposits a few atomic layers of CdSe and produces as an end product nanorods composed of Au, Cd and Se blocks. The structure and composition of these blocks has been confirmed by electron

microscopy (EM) and energy dispersive spectroscopy (EDS).

Single Au-CdSe-Au nanorod devices display a light dependent conductivity change (Figure 20A) and show increased conductivity when activated with white light. In a light modulation experiment a small bias of 1.0 V was applied to the single rod device and the photoresponse measured while slowly cycling the light. The photoresponse of a single Au-CdSe-Au nanorod device when excited by white light is shown in Figure 20-B. Though the light-dependent behavior is reversible, the relaxation of the photo-induced current back to dark current is slow (usually 5~15 seconds).



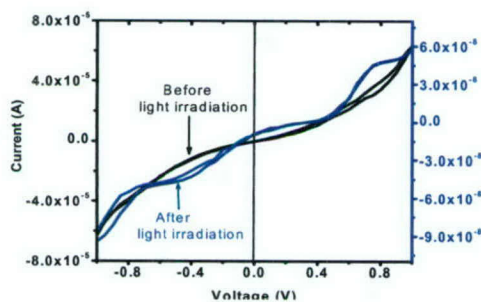
Currently studies are underway to investigate the photoresponse of Au-CdSe-Au nanorod devices as a function of temperature, wavelength and applied bias. Work by Heeger et al. describes an organic solar cell consisting of MEH-PPV conducting polymer



**Figure 20-B:** Change of current of a single Au-Cd-Se-Au nanorod at fixed bias ( $V=+1.5$  V). White light was modulated and cycled at  $\sim 0.1$  Hz (e.g. every 10 seconds).

V characteristics are irreversibly altered as well. In addition the experimental I-V and numerical  $dI/dV$  plots in Figure 23 suggest that in systems such as self-assembled metal nanocrystals Coulomb staircase characteristics do occur; thus the electrical behavior might be best characterized as an “ensemble Coulomb staircase”.

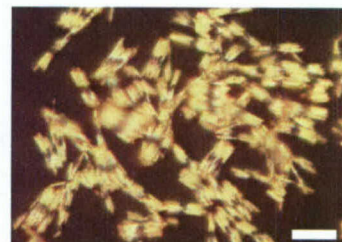
As the peak separations of the  $dI/dV$  plots (Figure 23) are relatively uniform, it is highly likely that the oscillatory steps in the I-V



**Figure 22:** I-V plots of single Au-Ppy-Ag-Au nanorods (room temperature). The pyrrole polymer is blended with  $C_{60}$  molecules.

blended with  $C_{60}$  molecules sandwiched between ITO glass and Al or Ca electrodes. Based on this research four-component nanorods composed of Au, Ag, and the conducting pyrrole polymer blended with  $C_{60}$  molecules, were fabricated. The fundamental electron transport properties of the blended  $C_{60}$ -conducting polymer material were investigated in order to use these materials for the fabrication of solar cells composed of multi-component conducting rod-like nanostructures.

Figure 22 illustrates that the overall shape of the I-V curves of four component nanorods upon activation by white light is irreversibly changed from non-linear Schottky-like to oscillatory



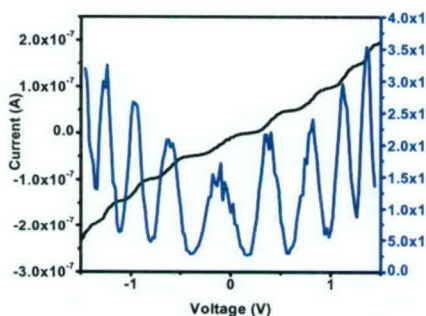
**Figure 21:** Optical microscopy image of Au-Ppy (blended with  $C_{60}$ )-Ag-Au nanorods. The size of the scale bar is 6 micron.

and the overall I-V curves (i.e. peaks in numerical  $dI/dV$  curves) are the result of the collective charging effect of the high density  $C_{60}$  molecules that generate many percolating conduction networks. Currently experiments are underway to further investigate and understand this “unorthodox” electrical behavior of the Au-Ppy(blended with  $C_{60}$ )-Ag-Au nanorods under the premise of an “ensemble Coulomb staircase”.



### 3.3. Triangular Nanoframes Made of Gold and Silver

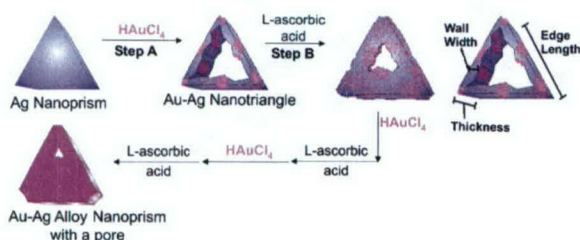
Silver nanoprisms ( $\sim 74$  nm edge length) can be etched with  $\text{HAuCl}_4$  to generate gold-silver alloy framework structures (Figure 24, Step A). While solutions of samples with low gold content ( $\text{Au}:\text{Ag} = 1:9$ ) were pale blue and displayed a low intensity, broad surface plasmon band at 775 nm, colloids containing high concentrations of gold ( $\text{Au}:\text{Ag} = 1:5, 1:3$ ) were pale gray (colorless) and displayed no strong surface plasmon bands in the UV-VIS spectrum (Figure 25A).



**Figure 23:** I-V (black) and numerical  $dI/dV$  (blue) plots of single Au-Ppy/ $\text{C}_{60}$ -Ag-Au nanorods at room temperature following activation with white light.

Transmission electron microscopy (TEM) images taken after addition of gold revealed the resulting nanostructures to be of triangular shape with hollow centers (Figure 25B-D). Measurements of wall width and thickness revealed that the wall width of the nanoframes increased slightly with increasing gold content. Experiments showed that increasing the gold to silver ratio from 1:9 to 1:3 led to nanoprisms with wall widths of 7.7 nm ( $\sigma = 11\%$ ) and 10.3 nm ( $\sigma = 21\%$ ), respectively. However, the

thickness of the gold-silver nanoframes (10 nm,  $\sigma = 20\%$ ) remained almost unchanged from the pure silver nanoprisms from which the Au-Ag nanoprisms were derived (9 nm).



**Figure 24: Synthetic pathway for triangular nanoframes made of Au or Ag.** Ag nanoprisms are etched with  $\text{HAuCl}_4$  (aq). Addition of L-ascorbic acid causes crystallization of Au and Ag on the inner walls of the nanoframes, the central pore shrinks in size. The gold salt/L-ascorbic acid cycle can be repeated to shrink the size of the central pore.

reaction, which reduced the gold and silver ions remaining in solution and deposited them onto the triangular nanoprism surfaces in a face-selective manner, reduced the size of the central pore. In these experiments, L-ascorbic acid was used to plate gold and silver onto the triangular nanoframes. This in turn thickened the walls and shrank the central pore (Figure 24, Step B).

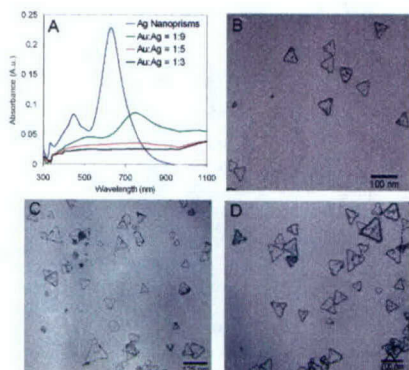
Subsequent additions of  $\text{HAuCl}_4$  followed by L-ascorbic acid (Figure 24, Steps A and B), led to a progressive reduction of the pore size, while at the same time the surface plasmon bands in the UV-VIS spectrum were regenerated. Since the backfilling process can be controlled, novel prisms with defined pore sizes can be formed.

TEM analysis at high magnification (200,000X) revealed that the center of each nanoprism was indeed hollow and the amorphous carbon film of the TEM support grid could be clearly seen in the underlying area. When these Au-Ag nanoprisms are backfilled with gold gold-silver alloy nanoprisms can be generated.

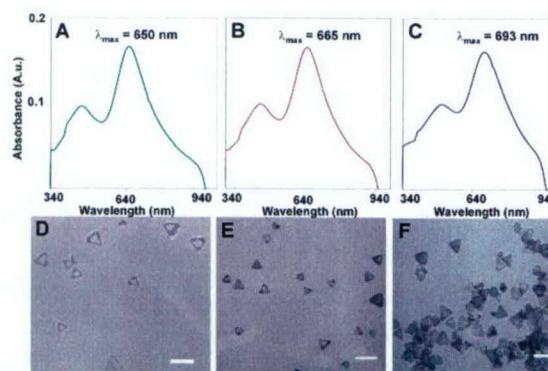
While analyzing the optical properties of these nanoframes a protocol was developed that allowed us to change the size of the central pore. Adding a mild reducing agent to the



This process therefore allows the fabrication of nanostructures such as truncated bimetallic nanoprisms, which cannot be synthesized via conventional photochemical or other synthetic routes. After two cycles, the pore size is decreased from 33 ( $\sigma = 23\%$ ) to 7 nm ( $\sigma = 14\%$ ) (Figure 26 E). After three gold/reduction cycles many of the nanoframes were completely filled, and the remaining particles possessed average pore sizes of 4 nm ( $\sigma = 13\%$ ) (Figure 26 F).



**Figure 25:** Gold-silver nanoframes. (A) UV-VIS spectra of nanoprisms with varying Au:Ag ratios. (B-D) TEM images of gold-silver nanoframes; (B) Au:Ag = 1:9; (C) Au:Ag = 1:5; (D) Au:Ag = 1:3. Scale bars in B and D are 100 nm, C 125 nm.



**Figure 26:** UV-VIS spectra and TEM images of backfilled Au:Ag nanoframes (Au:Ag ratio 1:9). (A, D) Addition of L-ascorbic acid. (B, E) 2 cycles of HAuCl<sub>4</sub>/L-ascorbic acid. (C, F) 3 cycles of HAuCl<sub>4</sub>/L-ascorbic acid. Note: More cycles will decrease the pore size. Scale bars in D and F are 100 nm, in E 125 nm.

## PERSONNEL SUPPORTED

### Postdocs:

Sung-Wook Chung  
Young Jo Kim

### % of Salary Support by Grant

100 % (2002, 2003, 2004)  
100% (2003)

### Graduate Students:

Emma Payne  
Emma Payne

### % of Salary Support by Grant

75% (2003)  
100% (2004)



**Unfunded Personnel:**

Nat Rosi (Postdoc)

Sungho Park (Postdoc)

**PUBLICATIONS****A. Journal Articles**

1. Li, Z.; Jin, R.; Mirkin, C.A.; Letsinger, R.L. "Multiple Thiol-Anchor Capped DNA Gold Nanoparticle Conjugates", *Nucleic Acids Res.* **2002**, *30*, 1558-1562.
2. Jin, R.; Wu, G.; Li, Z.; Mirkin, C.A.; Schatz, G.C. "What Controls the Melting Properties of DNA-Linked Gold Nanoparticle Assemblies?" *J. Am. Chem. Soc.*, **2003**, *125*(6), 1643-1654.
3. Li, Z.; Chung, S.W.; Nam, J.M.; Ginger, D.S.; Mirkin, C.A. "Living Templates for Hierarchical Assembly of Gold Nanoparticles", *Ang. Chem.* **2003**, *20*, 2408-2411.
4. Metraux, G.S.; Cao, Y.C.; Jin, R.; Mirkin, C.A. "Triangular Nanoframes Made of Gold and Silver", *Nano Lett.* **2003**, *3*, 519-522.
5. Jin, R.; Cao, Y.C.; Hao, E.; Metraux, G.S.; Schatz, G.C.; Mirkin, C.A. "Controlling Anisotropic Nanoparticle Growth Through Plasmon Excitation," *Nature* **2003**, *425*, 487-490.
6. Park, S.; Lim, J.H.; Chung, S.W.; Mirkin, C.A. "Self-Assembly of Mesoscopic Metal-Polymer Amphiphiles," *Science*, **2004**, *303*, 348-351.
7. Li, Z.; Zhang, Y.; Fullhart, P.; Mirkin, C.M. "Reversible and Chemically Programmable Micelle Assembly with DNA Block-Copolymer Amphiphiles," *Nano Lett.* **2004**, *4* (6), 1055-1058.
8. Rosi, N.; Thaxton, C.S.; Mirkin, C.A. "Control of Nanoparticle Assembly Using DNA- Modified Diatom Templates" *Angew Chem Int Ed.*, **2004**, *43*, 5500-5503.
9. Park, S.; Chung, S.W.; Mirkin, C.A. "Hybrid Organic-Inorganic, Rod-Shaped Nanoresistors and Diodes" *J. Am. Chem. Soc.*, **2004**, *126*, 11772-11773.

**B. Books and/or Book Chapters**

C.M. Niemeyer and C.A. Mirkin, *Nanotechnology: Concepts, Applications and Perspectives*. Weinheim, Germany: Wiley-VCH Verlag GmbH, 2004.

**INTERACTIONS****A. Presentations/Presentations at Meetings, Conferences, Seminars**

1. NSF Sensor Workshop, Arlington, VA: "The New Challenges of Chemical and Biological Sensing" (2002).
2. DOE Workshop, San Diego, CA: "Biomolecular Materials" (2002).
3. Gordon Research Conference, Electrochemistry, Ventura, CA: "Dip-Pen Nanolithography: Towards Combinatorial Nanotechnology" (2002).
4. 223<sup>rd</sup> ACS National Meeting, Orlando, FL: "Three dimensional assemblies formed via the Weak-Link Approach" (2002).
5. Particles 2002, Orlando, FL: "Ultrasensitive and Selective DNA and Protein-Based Detection by Nanoparticles" (2002).



6. Baekeland Awards Symposium and Presentation, Rutgers University, NJ: Keynote Speaker "Nanostructure-based Biodiagnostics" (2002).
7. NSF "Small Wonders: Exploring the Vast Potential of Nanoscience", Washington, D.C.: "Small is Different...From Materials to Medicine" (2002).
8. DARPA/MTO Advanced Lithography Program Review, New Orleans, LA: (2002).
9. International Symposium on Bioanalytical Chemistry and Nanotechnology, Hunan University, China, Keynote Speaker: "Nanoparticle Probes: A New Frontier in Biodetection" (2002).
10. Gordon Research Conference: Combinatorial Chemistry, Oxford, United Kingdom: "Dip-Pen Nanolithography and Combinatorial Nanotechnology" (2002).
11. Gordon Research Conference: Electronic Processes in Organic Mater, Salve Regina University, RI: "Dip-Pen Nanolithography and Combinatorial Nanotechnology" (2002).
12. University of Illinois, Urbana/Champagne CNST Lecture, Urbana, IL: "Massively Parallel Dip Pen Nanolithography: Towards Combinatorial Nanotechnology," (2002).
13. Washington University Chemistry Biology Interface Lecturer 2002, St. Louis, MO: "Nanoparticle-based Molecular Diagnostics: A New Frontier in Biodetection".
14. NSF "Approaches to Combat Terrorism", Washington, D.C.: (2002).
15. MRS 2002 Fall Meeting, Boston, MA: "Scanning Multiplexed Raman Detection of DNA, RNA, and Protein Targets with Nanoparticle Probes"; "Biodirected Synthesis of Functional Materials using Nanoscale Building Blocks" (2002).
16. Nanoimprint and Nanoprint Technology Conference, San Francisco, CA: "Dip-Pen Nanolithography: Towards Combinatorial Nanotechnology" (2002).
17. AFOSR Program Review Biometric, Biomaterial, and Biointerfacial Sciences Program, Hawk's Cay, FL: "Ultra-Sensitive and Selective Chip-Based Detection of DNA", and "Surface-Templated, Bio-Inspired Synthesis and Fabrication of Functional Materials" (2003).
18. PittCon Conference, Orlando, FL: "Building a High Tech Company in a University Environment", "Novel Nanoparticle-Based Approaches to High Sensitivity Biomolecule Detection" (2003).
19. ACS National Meeting, New Orleans, LA: "Nanoparticle-Oligonucleotide conjugates: A New Frontier in Biodiagnostics" (2003).
20. Stanford University Student Hosted Colloquium Lecturer, Palo Alto, CA: "Massively Parallel Dip-Pen Nanolithography: Toward Combinatorial Nanotechnology" (2003).
21. DARPA Advanced Lithography Program Review – Santa Fe, NM: "Parallel, Ultrafast Sub-100 Nanometer Dip-Pen Nanolithography" (2003).
22. Frontiers in Chemistry – Mostafa El-Sayed Symposium, Atlanta, GA: "Light Assisted Routes to Anisotropic Nanostructures" (2003).
23. University of California, Los Angeles, CA: CNSI Lecturer, "Massively Parallel Dip-Pen Nanolithography: Towards Combinatorial Nanotechnology" and "The Weak-Link Approach to Supramolecular Coordination Chemistry" (2003).
24. University of Tel Aviv, Tel Aviv, Israel: Symposium in Chemical Physics Lecturer, "Massively Parallel Dip-Pen Nanolithography: Toward Combinatorial Nanotechnology" (2003).



25. University of Texas-Austin, Austin, TX: Hollingsworth Lecturer, "Massively Parallel Dip-Pen Nanolithography: Toward Combinatorial Nanotechnology" (2003).
26. Dickinson College, Carlisle, PA: Metzgar-Conway Fellowship Lecturer, "Nanotechnology: Small Thinking or Thing Small" (2003).
27. University of Ottawa, Ottawa, Canada: University Lecturer 2003, "Massively Parallel Dip-Pen Nanolithography: Toward Combinatorial Nanotechnology" (2003).
28. Georgia Institute for Technology, Atlanta, GA: Molecular Design Institute Fall Lecture, "Nanostructures in Biodiagnostics: Will they make a difference?" (2003).
29. AFOSR MURI/DURINT Program Review, Dayton, OH (2003).
30. University of Wisconsin, Madison, WI: "Nanoparticle Probes: The Next Generation Molecular Diagnostic Indicators" (2003).
31. 226<sup>th</sup> ACS Meeting, New York, NY: "Nanoparticle Probes: the next generation molecular diagnostic indicators"; "Raman-Dye-Labeled Nanoparticle Probes for DNA, RNA, and Protein Detection" (2003).
32. Robert Wood Johnson Medical School "Biodefense" Seminar, Piscataway, NJ: "Nanoparticle-Based Biodiagnostics: Towards PCR-less Detection Methods" (2003).
33. NSF Workshop "Nanoscience and Engineering Education" Arlington, VA: "Overview and Perspective of Nanotechnology" (2003).
34. University of Toronto, Toronto, Canada: "Massively Parallel Dip-Pen Nanolithography: Towards Combinatorial Nanotechnology" (2003).
35. Indiana Biosensor New Ventures Conference, Indianapolis, IN: "Nanostructures in Biodiagnostics: Will they make a difference?" (2003).
36. 4<sup>th</sup> International Conference on Systems Biology, St. Louis, MO: "Ultrasensitive and Multiplexed Protein Detection with Nanoparticle-based Bio-barcodes" (2003).
37. University of Michigan - Symposium on Frontiers of Nanoscience and Nanotechnology, Ann Arbor, MI: "Nanostructures in Biodiagnostics: will they make a difference?" (2003).
38. MRS 2003 Fall Meeting, Boston, MA: "Functional Nanostructures via Dip-Pen Nanolithography" (2003).
39. Massachusetts Institute of Technology – Fall 2003 Nanostructures Lecture Series, Boston, MA: "Anisotropic Nanostructures: synthetic challenges assembly and biomedical applications" (2003).
40. Air Products Seminar, Allentown, PA: "Anisotropic Nanostructures: Synthetic Challenges, Assembly, and Biomedical Applications" (2003).
41. NSF Workshop "Japan – US Symposium on Directed Self-Assembly and Self-Organization" Santa Barbara, CA: "Self-Assembly of Anisotropic Structures" (2004).
42. AFOSR 2312 DX Program Review, Hawk's Cay, FL: "Surface Templated, Bio-Inspired Synthesis and Fabrication of Functional Materials," "Ultra-sensitive and Selective Chip-Based Detection of DNA" (2004).
43. AFOSR DPN Workshop, Hawk's Cay, FL: "State of the Art Applications and Future Challenges" (2004).



44. DARPA Advanced Lithography Program Review, Las Vegas, NV: "Massively Parallel Dip Pen Nanolithography" (2004).
45. 227<sup>th</sup> ACS National Meeting, Anaheim, CA: "Building Nanotech Companies in a University Environment," "DNA-mediated Assembly of Nanostructured Materials: Structure, Properties, and Biodetection Applications" (2004).
46. MRS 2004 Spring Meeting, San Francisco, CA: "Self-Assembly of Mesoscopic Amphiphiles," Combinatorial Nanotechnology through Massively Parallel DPN," "Ultrasensitive and Multiplexed Protein Detection with Nanoparticle-based Bio-barcodes" (2004).
47. NIAID Biodefense Workshop, Bethesda, MD: "Nanostructures in Biodiagnostics: Will they make a difference?" (2004).
48. Gordon Research Conference: Bioanalytical Sensors, Oxford, United Kingdom: Biomolecule Detection with Bio-barcodes: PCR-Like Sensitivity for Proteins, DNA, RNA, and Small Molecules (2004).
49. "Chips to Hits" IBC Conference, Boston, MA: "Nanostructures in Biodiagnostics: Will They Make a Difference?" (2004).
50. Korean Universities/Physical Society Series, Seoul, Korea: "Nanostructures in Biodiagnostics: A New Frontier in Medicine", Dip-Pen Nanolithography: Towards Combinatorial Nanotechnology", "Encoded Nanostructures for the Detection of Biomolecules" (2004).
51. NanoBio Summit, Cleveland, OH: "The Bio-Bar Code Assay: Towards PCR-like Sensitivity for Proteins, Nucleic Acids, Small Molecules, and Metal Ions" (2004).
52. AVS 51<sup>st</sup> International Symposium, Anaheim, CA: "The Bio-barcode Approach to Detecting DNA, Proteins, and Small Molecules" (2004).
53. MRS 2004 Fall Meeting, Boston, MA: "Massively Parallel Dip Pen Nanolithography" (2004).

#### **B. Consultative/Advisory Functions**

Chad Mirkin consults for NanoInk, Inc. and Nanosphere. He serves on the Scientific Advisory Board and the Board of Directors of both Nanosphere and NanoInk. He is one of the founding editors of the journal *Small*, and a member of the Editorial Advisory Boards of *Accounts of Chemical Research*, *Advanced Materials*, *Chemical and Engineering News*, *Macromolecular Bioscience*, *SENSORS*, *Encyclopedia of Nanoscience and Nanotechnology*, *Chemistry-A European Journal*, *Macro-Journals of Macromolecule*, *Chemistry & Biology*, *Nanotechnology Law & Business*, *Chemistry Worlds International Advisory Board (IAB)*, *Journal of Materials Chemistry*, *Nanotech Briefs* and *Chemistry World* of the Royal Society of Chemistry. Prof. Mirkin is also a member of the Science Advisory Board for the International Society for Nanoscale Science, Computation, and Engineering.

### **NEW DISCOVERIES, INVENTIONS, OR PATENT DISCLOSURES**

#### **A. New Discoveries**

1. Formation of nanotriangles from nanoprisms.



2. Formation of tubular and rod-like structures from metal-organic composite material building blocks.
3. Synthesis of polystyrene-DNA amphiphiles and formation of 3-D networks with gold nanoparticles.
4. Development of a procedure to covalently functionalize diatom cell walls with DNA; used the functionalized diatoms as templates for the 3-D assembly of gold nanoparticles.
5. Development of techniques to functionalize gold nanoparticles with DNA. Functionalized nanoparticles will self-organize in an aqueous medium into supramolecular gold nanoparticle assemblies.
6. Template-mediated electrochemical synthesis of metal-organic hybrid nanorods that selectively display resistor- or diode-like characteristics.

**B. Inventions and/or Patent Disclosures**

1. Mirkin, C.A.; Metraux, G.S.; Cao, Y.C.; Jin, R. "Triangular Nanoframes Made of Gold and Silver". Patent Application, 2004.
2. Mirkin, C.A.; Jin, R.; Cao, Y.C. "Cooperative, Photo-mediated Fusion of Silver Nanostructures". Patent Application, 2004.
3. Mirkin, C.A.; Zhi Li, Z. "Reversible and Chemically Programmable Micelle Assembly with DNA Block-Copolymer Amphiphiles. Provisional Application, 2004.
4. Chad A. Mirkin, C.A.; Park, S.; Chung, S.-W. "Hybrid Organic-Inorganic, Rod-Shaped Nanoresistors and Diodes". Provisional Application, 2004.
5. Mirkin, C.A.; Rosi, N.; Thaxton, C.S. "Diatoms as Chemically Modifiable Templates for the Assembly of Nanostructures". Provisional Application, 2004.

**7. HONORS/AWARDS**

1. Esquire Magazine's "Best & Brightest in the Nation" (NU, 2002)
2. 2002 Ceramographic Competition, American Ceramic Society 1<sup>st</sup> Place Entry (NU, 2002)
3. Forbes.com, The Forbes/Wolfe Nanotech Report, Mar 2003 "Nanotechnology's Top 10 Power Brokers" (NU, 2003)
4. 2003 Raymond and Beverly Sackler Prize in the Physical Sciences (NU, 2003)
5. 2003 Raymond and Beverly Sackler Prize in the Physical Sciences (NU, 2003)
6. Collegiate Inventors Award, National Inventors Hall of Fame (NU, 2003)
7. Dickinson College Metzger-Conway Fellowship Award (NU, 2003)
8. ACS Nobel Laureate Signature Award for Graduate Education in Chemistry (NU, 2003)
9. Dickinson College Honorary Degree (NU, 2004)
10. Pennsylvania State University Outstanding Science Alumni Award (NU, 2004)
11. Collegiate Inventors Award, National Inventors Hall of Fame (NU, 2004)
12. NIH Director's Pioneer Award (NU, 2004)